ELSEVIER

Catalysis Today 29 (1996) 251-254

CATALYSIS TODAY

Activation of off site presulfided Cobalt–Molybdenum catalysts

P. Dufresne [a,*], N. Brahma [a], F. Labruyère [b], M. Lacroix [b], M. Breysse [b]

[a] EURECAT, Quai Jean Jaurès, BP 45, 07800 La Voulte sur Rhône, France
[b] Institut de Recherches sur la Catalyse, 2 Avenue Albert Einstein, 69626 Villeurbanne cedex, France

Abstract

An oxidic Co–Mo catalyst presulfided by the SULFICAT® process has been studied by XPS. Results indicate that the strong interaction of the alkylpolysulfide with the solid provokes a partial reduction of both the sulfur and molybdenum ions. Treated under hydrogen, the adsorbed species decompose at temperatures as low as 160–220°C converting the initial Mo^{6+} species into sulfided Mo^{4+}. The sulfidation state of the active phase increases with the hydrogen pressure. Comparison with the conventional sulfiding procedure indicates that the SULFICAT® process results in a higher dispersion of the sulfided active phase.

Keywords: SULFICAT process; Co–Mo catalysts

1. Introduction

The main purpose of the hydrotreating of petroleum feedstocks is the catalytic conversion of sulfur and nitrogen compounds into hydrocarbons, hydrogen sulfide and ammonia. Typically, the elimination of such contaminants requires hydrogen pressures of about 1–10 MPa and a temperature range comprised between 300 and 400°C. In general, sulfides of hydrogenating metals are utilized for hydro-desulfurization and hydro-denitrogenation and particularly catalysts containing cobalt or nickel and molybdenum or tungsten are used on a commercial basis. Such kind of catalysts are commercially available in their oxidic form and introduced into the unit in such a way. In order to reach their optimal activity, hydrotreating catalysts have to be sulfided. This sulfidation step is very important since the activity of the catalysts was found to be sensitive to the mode of sulfiding. Industrially this activation step is conducted in situ under hydrogen pressure by the feed itself or with a light gas-oil spiked with a sulfur containing molecule which liberates H_2S at moderate temperatures, i.e., CS_2, RSH or CH_3SSCH_3 (DMDS). Recently, a process which transforms the inactive oxide state into a stable intermediate form has been patented by EURECAT [1,2]. The SULFICAT® process consists in 'wetting' ex situ the supported oxides with an alkylpolysulfide. After a thermal treatment step, the catalyst can be loaded in the refinery unit and efficiently activated without requiring any sulfur addition. The final sulfidation of the 'presulfided catalyst' is completed in situ during the start-up procedure performed under hydrogen pressure and in the presence of the hydrocarbon liquid phase. The aim of this work was to characterize the presulfided solid and to study

---

[*] Corresponding author.

SSDI 0920-5861(95)00280-4

the influence of the hydrogen pressure on the decomposition of the organic polysulfide. For this purpose, several techniques were used, i.e., temperature programmed reduction (TPR), XPS and catalytic activity measurements.

2. Experimental

The solid studied in this work is an industrial Co–Mo/Al_2O_3 treated by EURECAT. The oxidic phases were presulfided with a commercial ditertiononyl pentasulfide (TNPS) containing about 37 wt.-% of sulfur. The amount of polysulfide deposited onto the catalyst was calculated in order to convert the oxidic Co and Mo phases into CoS and MoS_2. The activation was performed by heating the solid under hydrogen from room temperature up to 350°C (heating rate 4°C/min). This procedure was carried out in a stainless steel plug flow microreactor under various hydrogen pressures. The heated part of the set up contains an inner quartz tube in which the catalyst was placed in order to prevent any consumption of the formed H_2S by reaction with the heated walls of the reactor. The gas phase composition was analyzed by means of a mass spectrometer (FISONS Instruments) equipped with a quadrupole analyser (VG analyzer) working in a Faraday mode. A silica capillary tube heated at 180°C continuously bled off a small fraction of the gas phase into the spectrometer. In a typical TPR run, the more intense m/e signals were recorded: H_2S (34), C_3H_7 (43), C_4H_9 (57) and C_5H_{11} (71).

XPS measurements were carried out with a ESCALAB 200R FISONS using an aluminum (Al $K\alpha = 1487$ eV) X-ray source. Binding energies are given by reference to C 1s at 284.5 eV as internal standard. Dispersion (*D*) was calculated after subtracting non-linear Shirley background. Non-linear least squares curve fitting method based on the Marquardt–Levenberg algorithm was used for calculating the distribution of the oxidation states of a given element. The same Co–Mo precursor was sulfided at 400°C by H_2–H_2S. This sample was utilized as reference for the XPS measurements.

The catalytic properties of the different activated solids were determined at 300°C using the thiophene hydro-desulfurization as model reaction. The experiments were performed at atmospheric pressure using 2.5 mol.-% of thiophene diluted in hydrogen. Conversions were kept lower than 15% in order to avoid mass transfer limitations.

3. Results

The S 2p XPS spectra of the sulfided Co–Mo catalyst and of the TNPS adsorbed on alumina support and on the oxidic Co–Mo catalyst are reported in Fig. 1. For the sulfided solid, the S 2p binding energy (BE) was detected at 161.4 eV in accordance with the presence of S^{2-} species currently observed on MoS_2. The S 2p BE of TNPS adsorbed on the alumina support found at 163.6 eV agrees with the data reported by Lindberg et al. for organic compounds containing –C–S–C– and –C–S–S–C– bonds [3].

On the Co–Mo phase, this photopeak shifts towards lower BE (162.9) suggesting that during impregnation and drying the interaction of the alkyl polysulfide with the surface of the solid partially reduces the sulfur atoms initially present as –S_5– chain. Fig. 2 evidences that the TNPS deposit also modifies the molybdenum oxidation state. As a matter of fact, the Mo 3d envelope of the initial oxide Co–Mo catalyst

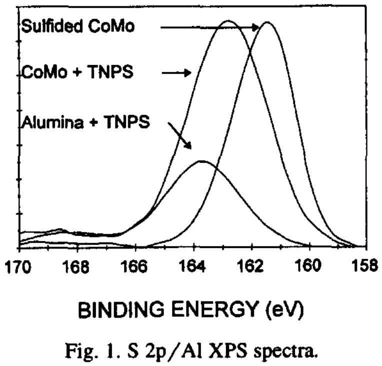

Fig. 1. S 2p/Al XPS spectra.

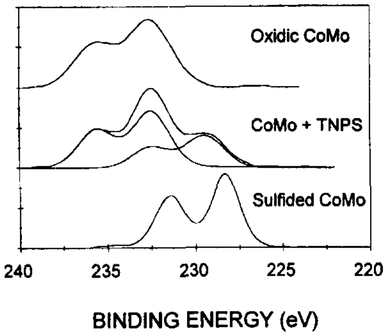

Fig. 2. Mo 3d/Al XPS spectra.

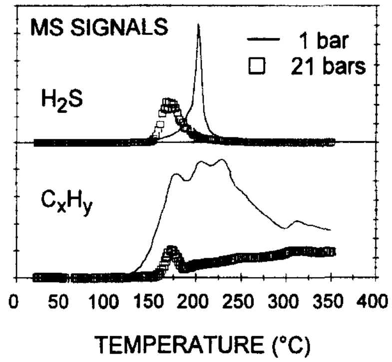

Fig. 3. H_2S and C_xH_y TPR profiles of the TNPS impregnated Co–Mo catalyst.

can be curve fitted as a single doublet with BE values characteristic of Mo^{6+} (Mo $3d_{3/2}$: 235.3 eV, Mo $3d_{5/2}$: 232.2 eV) while for the impregnated solid fitting required an additional doublet with Mo $3d_{5/2}$ BE value at 229.1 eV which cannot be assigned to the presence of sulfided Mo^{4+} species (BE at 228.4 eV). By comparison with results obtained by Yusamaru et al., this species seems to be related to a Mo^{4+} in an oxygen environment [4]. Therefore, the TNPS molecule is strongly bonded and probably decomposed on the Co–Mo phase.

Temperature programmed reduction of this solid leads mainly to the formation of H_2S and hydrocarbons denoted by C_xH_y (Fig. 3). Upon hydrogen treatment, the catalyst releases both H_2S and hydrocarbons at the same temperature which corresponds to the decomposition of the adsorbed TNPS species.

An increase of the hydrogen pressure provokes an increase of the decomposition rate since the temperature which corresponds to peak maxima is shifted by about 50°C. Moreover the amount of H_2S evolved from the solid surface under 21 bar is lower than at atmospheric pressure suggesting that sulfidation is pressure favoured. This assumption is consistent with the XPS data represented in Fig. 4 and reported in Table 1. As previously mentioned, the Mo 3d XPS signal of the initial solid contains both oxidic Mo^{6+} and Mo^{4+} species. The solid treated at atmospheric pressure the Mo 3d signal can be decomposed into three different species with maxima Mo $3d_{5/2}$ BE at 228.4, 230.6 and 232 eV, respectively. The photopeak at 228.4 eV represents the fraction of sulfided molybdenum species (Mo^{4+}) while the higher energy peak corresponds to Mo^{6+} in an oxygen environment. The third species (230.6 eV) is indicative of the presence of an intermediate oxidation state whose identification is still not completely elucidated. According to Yasumaru et al., this entity may correspond to an intermediate Mo^{5+} species coordinated to oxygen anions [4]. How-

Table 1
Quantitative XPS data and catalytic properties as a function of the activation procedure (Mo_t: total Mo 3d XPS signal, Mo_S: sulfided Mo^{4+} species)

Catalyst	$D = \frac{Mo_t}{Al} \times (10^2)$	$\frac{Mo_S^{4+}}{Al} \times (10^2)$	Specific activity (μmol/s g)
Initial catalyst	10	0	–
Activity at 1 bar	8.3	5.56	1.3
Activity at 21 bar	8.4	6.38	2
Activity at 21 bar + recycling	7.9	6.39	2.1
Sulfided by H_2/H_2S	6.8	5.64	1.2

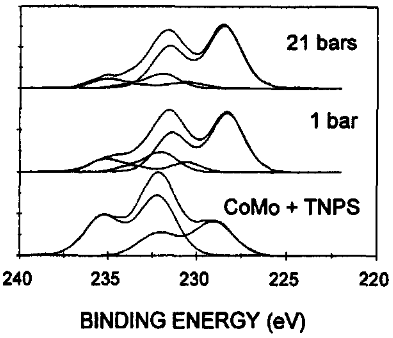

Fig. 4. Mo 3d/Al XPS spectra.

ever, the presence of oxysulfide –S–Mo^{6+}–O– species or $MoO_2S_2^{2-}$ like complexes cannot be excluded since Arnoldy et al. found that low temperature sulfidation proceeds via an O–S exchange reaction [5] and the replacement of some oxygen atoms by less electronegative sulfur ions should decrease the BE of Mo^{6+} species. The main pressure effect consists in an increase of the concentration of sulfided Mo species at the expense of the Mo–O species. These results correlate fairly well with the catalytic properties of these solids reported in Table 1.

According to these data, both the sulfidation state and the catalytic activity of the solid activated at 21 bar are higher than when sulfided by H_2/H_2S at the same temperature (350°C). However, Fig. 3 indicates that a fraction of the sulfur is released by the system and therefore cannot participate in the sulfidation of the catalyst. During the startup procedure, the gas phase is often recycled. In order to simulate recycling, a small concentration of H_2S was added into the feed from 160 up to 350°C. The amount of sulfur introduced into the system was adjusted in order to compensate for the amount lost during the activation procedure under pure hydrogen (hydrogen pressure 21 bar). As a matter of fact, this procedure effectively increased the S/Mo ratio but a concomitant loss of the Mo_t dispersion was detected. Accordingly, the dispersion of the sulfided Mo^{4+} becomes comparable to the one reported without recycling. Moreover, data reported in Table 1 also evidence that a better dispersion of the active phase is observed for the solids activated by the SULFICAT® process. Therefore the better thiophene HDS activity of the SULFICAT® sample could be ascribed to this high dispersion.

4. Conclusions

The interaction of an alkylpentasulfide with the surface of an industrial Co–Mo catalyst is strong enough to partially reduce both sulfur and molybdenum species. Upon hydrogen, the adsorbed organic species decompose at a temperature as low as 160–210°C depending of the hydrogen pressure. This decomposition step transforms the presulfided solid into the active Co–Mo–S phase. XPS characterization of the sulfided solid indicates that the active phase is well dispersed over the alumina support and this sulfiding procedure leads to more active catalysts than those activated by conventional sulfidation methods.

References

[1] G. Berrebi, Eur. Patent 0130650, 1984.
[2] S.R. Murff, E.A. Carlisle, P. Dufresne and H. Rabehasaina, Preprints Am. Chem. Soc., Div. Petrol. Chem., 38(1) (1993) 81.
[3] B.J. Lindberg, K. Hamrin, G. Johasson, U. Gelius, A. Fahlman, C. Nordling and K. Siegbahn, Phys. Scripta, 1 (1970) 286.
[4] J. Yasumaru, M. Yamada, M. Houalla and D.M. Hercules, Proc. 10th Int. Congr. Catal., B (1993) 1867.
[5] P. Arnoldy, J.A.M. van den Heijkant, G.D. de Bok and J.A. Moulijn, J. Catal., 92 (1985) 35.